Profiles of Stratospheric Chlorine Nitrate ($ClONO_2$) from ATMOS/ATLAS 1 Infrared Solar Occultation Spectra

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Abstract

Stratospheric volume mixing ratio profiles of chlorine nitrate ($C\ell ONO_2$) have been retrieved from 0.01-cm^{-1} resolution infrared solar occultation spectra recorded at latitudes between 14°N and 54°S by the Atmospheric Trace Molecule Spectroscopy (ATMOS) Fourier transform spectrometer during the ATLAS 1 shuttle mission (March 24 to April 2, 1992). The results were obtained from nonlinear least-squares fittings of the $C\ell ONO_2$ ν_4 band Q branch at 780.21 cm^{-1} with improved spectroscopic parameters generated on the basis of recent laboratory work. The individual profiles, which have an accuracy of about ±20%, are compared with previous observations and model calculations.

1. Introduction

The second flight of the Atmospheric Trace Molecule Spectroscopy (ATMOS) Fourier transform spectrometer as part of the Atmospheric Laboratory for Applications and Science (ATLAS)-1 shuttle mission (March 24-April 2, 1992) [Gunson, 1992] provided the opportunity to obtain sets of nearly simultaneous concentration measurements of over two dozen stratospheric molecules about 9½ months after the massive eruption of the Mt. Pinatubo volcano in the Philippine Islands and 6 years and 11 months after the first ATMOS flight onboard Spacelab 3 [Farmer, 1987; Farmer et al., 1987]. Of prime scientific interest are the measurements of trace gases involved in stratospheric ozone chemistry. In this paper, we report ATMOS/ATLAS 1 stratospheric volume mixing ratio (VMR) profiles of chlorine nitrate ($C\ell ONO_2$), an important diurnally varying chlorine reservoir inhibiting ozone destruction by the $C\ell O_x$ catalytic cycle. Comparisons of these results with previous measurements and model calculations are also reported.

2. Observations

During the ATLAS-1 shuttle mission, the ATMOS Fourier transform spectrometer recorded ~10,000 two-sided solar interferograms with a maximum path difference of 47.5 cm. The spectra derived from processing these interferograms have an unapodized resolution of ~0.01 cm^{-1}. The measurements were obtained from an orbital altitude of ~300 km during 53 sunrises occurring between 30°N and 32°S latitude and 41 sunsets observed between 22°S and 54°S latitude. The 2.2-s intervals between successive observations corresponded to tangent height separations of ~2.5 km in the mid-stratosphere. The intensities in the atmospheric spectra were divided at each wavelength by the corresponding values in an exoatmospheric spectrum obtained by averaging all the high sun spectra recorded during the same occultation. This ratioing procedure removed the wavelength dependence of the instrument-filter-detector system response and solar features as well as H_2O and CO_2 lines produced by residual air within the interferometer. Additional information about the ATMOS instrument, its operation and performance, and ATMOS data processing and analysis procedures is given in the papers by Farmer [1987], Farmer et al. [1987], Norton and Rinsland [1991], and Gunson [1992].

The $ClONO_2$ VMR profiles reported here were retrieved from the seven sunrise and seven sunset occultations recorded with filter 1 spanning the 600-1190-cm^{-1} domain. The spectra obtained with this filter have the best signal-to-RMS noise ratio (~250) in the 780-cm^{-1} region where the most favorable $ClONO_2$ absorption feature for quantitative analysis is located. Table 1 summarizes the key parameters for the 14 occultation events studied in this work. Note that the stratospheric coverage of the tropical (sunrise) occultations is limited to tangent heights above ~27 km because the ATMOS suntracker, which senses near IR light, could not acquire the sun at lower altitudes where the attenuation by the Mt. Pinatubo aerosols was very high.

3. Spectroscopic Parameters

For the first time, $ClONO_2$ profiles have been retrieved with a line list based on a quantum mechanical calculation. The list was computed by one of us (A.G.) with the molecular constants reported by Bell et al. [1992] for the ν_4 $^{35}ClONO_2$ band at 780.21 cm^{-1}, the ν_4 $^{37}ClONO_2$ band at 778.86 cm^{-1}, and the $\nu_4 + \nu_9 - \nu_4$ $^{35}ClONO_2$ band at 778.73 cm^{-1}.

The intensities in the $ClONO_2$ line list were calculated assuming the bands are noninteracting and by normalizing the intensities on the basis of laboratory data. First, a terrestrial $^{35}C\ell/^{37}C\ell$ isotope ratio of 3.086 was assumed in computing the relative intensities of the ν_4 bands of $^{35}C\ell ONO_2$ and $^{37}C\ell ONO_2$. Next, the relative intensity of the $^{35}C\ell ONO_2$ hot band with respect to the other two bands was adjusted to match the relative band strengths in a 0.002-cm^{-1} resolution laboratory spectrum recorded at room temperature [Goldman et al., 1989, Fig. 8, spectrum C]. The $C\ell ONO_2$ volume mixing ratio in the laboratory sample was then determined by comparing the integrated intensity in the 750-830-cm^{-1} region with values reported in the literature [Davidson et al., 1987; Ballard et al., 1988; Tuazon and Wallington, 1989] and by fitting the $^{35}C\ell ONO_2$ Q branch in the laboratory spectrum with the empirical line parameters of Ballard et al. [1988]. The standard deviation of these four VMR determinations is $\pm 8\%$. Finally, assuming the mean VMR as the correct value for the laboratory sample, a factor to scale the relative intensities in the line list to absolute values was derived by least-squares fitting the laboratory spectrum in the $^{35}C\ell ONO_2$ ν_4 Q branch region with the new line parameters. The derived intensity scaling factor is estimated to be accurate to about $\pm 12\%$. The sum of the intensities in units of cm^{-1}/(molecule-cm^{-2}) at 296 K and the number of lines in the list are 1.439×10^{-18} and 11495 for the ν_4 band of $^{35}C\ell ONO_2$, 4.656×10^{-19} and 10211 for the ν_4 band of $^{37}C\ell ONO_2$, and 9.191×10^{-19} and 10493 for the $\nu_4 + \nu_9 - \nu_9$ hot band of $^{35}C\ell ONO_2$, respectively.

The average room temperature N_2-broadening coefficient of 0.14 cm^{-1} atm^{-1} measured in the ν_4 band $^{35}C\ell ONO_2$ Q branch [Bell et al., 1992] has been adopted at 296 K for the atmospheric retrievals along with a $T^{-0.75}$ temperature dependence for the line widths. Simulations with the new line list do not reproduce the rotational fine structure observed near 780.15 cm^{-1} in the low pressure laboratory spectra [e.g., Goldman et al., 1989, Fig. 8], but published plots of unable diode laser spectra broadened by N_2 show that this structure within the $^{35}C\ell ONO_2$ ν_4 band Q branch is barely noticeable above a total pressure of 10 mb and completely disappears at 30 mb [Bell et al., 1992, Fig. 4]. Therefore, errors in simulating the $C\ell ONO_2$ Q branch fine structure are small for stratospheric paths containing significant $C\ell ONO_2$ absorption.

The spectroscopic line parameters for all other molecules were taken from an updated version (L. R. Brown, private communcation, 1993) of the ATMOS compilation Brown et al., 1987 . Except for $C\ell ONO_2$, the ATMOS line list in the region analyzed here is essentially the same as listed in the 1992 HITRAN compilation [Rothman et al 992]

4 Analysis and Results

The $C\ell ONO_2$ profiles reported here were retrieved with the ODS (Occultation Display Spectrum) program, an onion-peeling, nonlinear least-squares spectral fitting algorithm developed at the Jet Propulsion Laboratory (JPL) [Norton and Rinsland, 1991]. The $C\ell ONO_2$ results have been compared to retrievals performed with another algorithm independently developed a the NASA Langley Research Center (LaRC) [Rinsland et al., 1991] and based on a "global-fitting" approach (simultaneous fitting of a set of microwindows in all spectra). These intercomparisons resulted in $C\ell ONO_2$ volume mixing ratios in agreement to about 7% at tangent heights below 30 km and about ±12% at 34 km (1 sigma) when the same physical model and spectroscopic line parameters are adopted. Both retrieval algorithms include corrected $C\ell ONO_2$ vibrational partition function calculations [Zander et al. 1990; Norton and Rinsland, 1991].

The pressure-temperature profiles assumed in the analysis were derived directly from the spectra using a procedure developed by G. P. Stiller (manuscript in preparation, 1994). Briefly, the ODS algorithm is used to perform independent, onion-peeling CO_2 VMR retrievals from ~100 narrow intervals, each centered on an isolated CO_2 line. The tangent layer CO_2 VMRs retrieved from each spectrum are then least-squares fitted as a function of the CO_2 line lower state energy to determine corrections to initial guesses for the rotational temperature (which is assumed to equal the kinetic temperature) and the atmospheric pressure in the layer. A CO_2 profile equal to a constant VMR of 3.47×10^{-4} in the lower stratosphere increasing to 3.54×10^{-4} in the troposphere has been assumed for the 1992 ATMOS/ATLAS 1 mission. This iterative procedure converges rapidly and results in pressures with estimated precisions of 5% below 35 km and 3% up to 70 km and temperatures with precisions of 1 to 2 K.

The $C\ell ONO_2$ profiles were derived from fittings over a 0.6-cm^{-1} wide microwindow centered on the $^{35}C\ell ONO_2$ ν_4 band Q branch at 780.21 cm^{-1}. The primary interferences in this interval are O_3 and CO_2 lines with weaker absorptions from lines of the ν_8 band of HNO_3 [Goldman et al., 1989; Zander et al., 1990]. In the ODS retrievals, the O_3 profile was first retrieved and then held fixed during the analysis for $C\ell ONO_2$ while simultaneous fittings for the profiles of both molecules were performed with the LaRC algorithm. Sensitivity tests indicate that realistic differences in the assumed HNO_3 profile have a negligible (<2%) effect on the retrieved $C\ell ONO_2$ profile.

Figure 1 shows a comparison of least-squares fits obtained with the new $C\ell ONO_2$ line parameters and the empirical $C\ell ONO_2$ line parameters [Ballard et al., 1988] used in the ATMOS Spacelab 3 retrievals [Zander et al., 1990, 1992]. The new list produces slightly better fittings to the ATMOS spectra than the old list, both near the peak of the $C\ell ONO_2$ Q branch where more absorption is now predicted and in the low wavenumber wing of the Q branch where less absorption is now predicted (the same improvements have been noted from least-squares fits to the University of Denver $ClONO_2$ laboratory spectra).

No obvious differences were found among the six tropical sunrise profiles between 15.7° N and 16.7° S latitude or among the seven sunset profiles recorded between 44.5° S and 55.4° S latitude. Therefore, in Table 2 we report mean profiles for these two latitude bands along with a separate entry for the sunrise (SR) occultation SR03 at 28.2° S latitude.

The sources of random (R) and systematic (S) error and the 1-sigma uncertainty in the $ClONO_2$ VMR resulting from each error source are (1) instrumental effects (R), primarily due to the finite signal-to-noise ratio, ±8% at 20 to 30 km increasing to ±20% at 35 km; (2) the tangent pressure (R), ±5%; (3) the temperature profile (R), ±1%; (4) the assumed $ClONO_2$ line parameters (S), ±12%; (5) the CO_2 parameters assumed in the pressure-temperature retrieval (S), ±3%; (6) the assumed CO_2 volume mixing ratio profile (S), ±2%; and (7) the simulation of interfering spectral absorptions (R), ±5% at 20 to 30 km increasing to ±10% at 35 km. A total 1-sigma error of ±16% at 20 to 30 km increasing to ±26% at 35 km and a 1-sigma precision of ±11% at 20 to 30 km increasing to ±23% at 35 km for a single profile have been computed from the square root of the sum of the squares of the individual errors. The errors listed between parentheses in Table 2 assume that the magnitude of the random errors is reduced by the square root of the number of averaged retrievals.

5. Discussion

No tropical $ClONO_2$ profile measurements have been reported prior to the present work. However, the southern hemisphere ATLAS 1 zonal mean sunset profile can be compared with the May 1985 Spacelab 3 sunrise profile at 47° S latitude. For consistency, we reanalyzed the Spacelab 3 data with the new $C\ell ONO_2$ linelist and a pressure-temperature profile retrieved with the algorithm described earlier. The upper panel of Figure ? shows these two measured profiles.

The lower panel of Figure 2 presents three sets of $C\ell ONO_2$ profiles calculated for 47°S latitude with the Atmospheric. and Environmental Research, Inc. (AER) two dimensional chemistry-transport model [NASA, 1993, Chap. 4]. The solid curves are model sunset profiles for day 90 of 1992 (appropriate for the ATLAS 1 mission observations), the long dashed curves are model sunrise profiles for clay 120 of 199?, and the snort dashed curves are model sunrise profiles for clay 1?0 of 1985 (appropriate for the Spacelab 3 mission observations). Stratospheric total inorganic chlorine abundances at 5.25, 14.3, 38.8, and 63.9 mb We're 3.?8, 3.05, ?.00, and 1.28 ppbv (parts per billion, 10^{-9} by volume) for the 199? calculations and ?.45, ?.30, 1.51, and 0.94 ppbv for the 1985 calculations, respectively. The three curves for each 199? elate represent talc.ulations for gas phase chemistry only, heterogeneous chemistry with background aerosol levels [World Meteorological Organization (WMO), 199?, Table 8-8], and heterogeneous chemistry with the volcanic aerosol surface area profiles derived from Stratospheric Aerosol and Gas Experiment (SAGE II) measurements ((; . K. Yue, private communication, 1993). The two curves for 1985 show calculations with gas phase chemistry only and heterogeneous chemistry at background aerosol levels.

The heterogeneous chemistry calculations include two reactions:

$$N_2O_5 + H_2O \rightarrow HNO_3 + HNO_3 \qquad (1)$$

$$C\ell ONO_2 + H_2O \rightarrow HNO_3 + HOC\ell \qquad (?)$$

The parameterization for reaction 1 is described by Rodriguez et al. [1991] with an assumed reaction probability per reaction of 0.1. The parameterization for reaction 2 is given in NASA [1993]. Laboratory studies [Tolbert et al., 1988; Hanson and Ravishankara, 1991] indicate low probabilities for reaction (2) in the nonpolar stratosphere. The effect of this reaction on the AER model results shown in Figures 2 and 3 is small.

Three conclusions can be drawn from the results in Figure 2. First, comparison of the solid curves in the lower panel shows that the inclusion of heterogeneous chemistry with the volcanic aerosol levels occurring during the ATLAS 1 mission changes the calculated $C\ell ONO_2$ volume mixing ratios by less than 10% at 47° S latitude for 5 to 40 mb. Second, comparison of the solid and long dashed model curves in the lower panel shows that changes in the $C\ell ONO_2$ volume mixing ratio due to the combined diurnal and seasonal differences between the Spacelab 3 and ATLAS 1 missions are small for altitudes below 30 km. The small diurnal change in $C\ell ONO_2$ below 30 km agrees with previous model calculations [Ko and Sze, 1984, Fig. 6]. Third, the measured $C\ell ONO_2$ profiles for both 1985 and 1992 are significantly lower than the corresponding model profiles with the largest relative differences occurring near the VMR peak. The measured ATLAS 1 profile has a peak $C\ell ONO_2$ mixing ratio of 0.94 ± 0.16 ppbv at 16 mb whereas the corresponding AER model sunset profile computed with heterogeneous chemistry and the ATLAS 1 volcanic aerosol levels reaches a maximum of 1.56 ppbv at 14.3 mb.

Although the absolute values are significantly different, the measured 1992-to-1985 $C\ell ONO_2$ ratios at 47° S latitude are in better agreement with the corresponding model predictions. Adopting the 1992 day 90 sunset calculations with the volcanic aerosol levels for the ATLAS 1 mission and the 1985 day 120 sunrise background heterogeneous chemistry calculations for the Spacelab 3 mission, we derive model 1992 sunset to 1985 sunrise $ClONO_2$ ratios of 1.18, 1.31, 1.30, and 1.39 at 10, 16, 30, and 50 mb, respectively, whereas the measured ratios (and 1-sigma uncertainties) at the same pressure levels are 1.36±0.16, 1.30±0.15, 1.49±0.17, and 1.12±0.13, respectively.

Figure 3 shows the mean tropical sunrise profile from the ATLAS 1 mission and the corresponding AER model predictions with heterogeneous chemistry and the March 1992 aerosol levels. Again, the measurements are systematically lower than the model calculations with the largest discrepancies occurring near the VMR peak. The May 1985 ATMOS/Spacelab 3 $ClONO_2$ 30° N sunset profile [Zander et al., 1990, 1992] is uniformly lower by about a factor of 1.5 than profiles calculated by five modeling groups for the same conditions [NASA, 1993, Chap. 5, section M]. A revised retrieval obtained with the new $ClONO_2$ lineIist and an improved temperature profile slightly increases the discrepancies. These model-measurement differences are significant given the important role of $ClONO_2$ in buffering O_3 destruction. Natarajan and Callis [1991] found that a secondary path for the reaction OH + ClO, leading to the production of HCl, would improve the agreement between their model calculations and the Spacelab 3 measurements of $ClONO_2$ and HCl.

Recently, Webster at al. [1993] estimated $ClONO_2$ volume mixing ratios in the northern hemisphere mid- to high-latitude lower stratosphere based on N_2O and HCl measurements obtained during December 1991 and March 1992 aircraft flights outside of polar stratospheric cloud (PSC)-processed regions. Their inferred $ClONO_2$ VMRs are about a factor of 2 higher than the ATMOS/ATLAS 1 values corresponding to the same N_2O volume mixing ratio. A detailed analysis of stratospheric chlorine partitioning based on ATMOS/ATLAS 1 measurements including additional chlorine-bearing species, particularly $HC\ell$, and important chemically-linked species (e.g., CH_4, which affects the $HC\ell$ distribution) will be reported in the near future (M. R. Gunson, manuscript in preparation, 1994).

Acknowledgments. Research at the Jet Propulsion Laboratory (JPL), California Institute of Technology, is performed under contract to the National Aeronautics and Space Administration. Research at the University of Liège was partially supported by Belgian funds through the Services de la Programmation et de la Politique Scientifique, Brussels. Acknowledgment is made for help in data processing provided by members of the ATMOS data processing team at JPL, J. Wilding of Science Applications International Corporation (SAIC), Hampton, Virginia, and R. Sip of the University of Liège.

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Table 1. ATMOS/ATLAS 1 Occultations Analyzed in this Study

Occultation Name*	Date, UT	Latitude,†	Longitude,†	Minimum Tangent Height (km)
		sunsets		
SS25	March 29, 1992	44.5°S	251 .?″ Ii	?1.1
SS26	March 29, 1992	46.2°s	92.5°E	22.1
SS31	March 29, 1992	47.7°S	293.9° E	19.9
SS37	March 30, 1992	50.6°S	336.5° E	10.5
SS41	March 31, 1992	51.0°s	245.9° E	18,8
SS43	April 1, 199?	53.6°S	130.3° E	19.7
ss48	April 2, 1992	55.4°S	241 .0°E	?1.9
		Sunrises		
SR03	March 25, 1992	28.2°S	300.8° E	5
SR09	March 26, 1992	16.7°S	184.9°E	29.2‡
SR26	March ?8,]992	0.6°s	202.3°E	28.4
SR31	March ?9, 1992	3.2°N	89.0°E	27.3
SR35	March ?9, 1992	8.2°N	222.3°E	27.1
SR37	March 29, 199?	9.2°N	177.0°E	26.9
SR44	March 30, 1992	15.7°N	219.8°E	27.1

*SS denotes sunset; SR, sunrise. The data were recorded with a 2.8-mrad diameter field of view corresponding to a 5.5-km vertical altitude range at the tangent point.

†Tangent point location at a tangent altitude of 30 km.

#A few additional spe ct ra were recorded in the troposphe re.

Table 2. ATMOS/ATIAS 1 $C\ell ONO_2$ Retrieval Results§

Pressure (mb)	Approximate Altitude (km)	$C\ell ONO_2$ Volume Mixing Ratio, 10^{-9} 15.7°N-16.7°S†	28.2°S*	44.5°S-55.4°S‡
4	37.8	0.30(8)	0.31(10)	0.21(6)
5	36.2	0.46(10)	0.49(13)	0.32(8)
7	33.8	0.63(13)	0.7?(16)	0.57(11)
10	31.4	0.78(15)	1.0?(18)	0.81(14)
1G	28.2	0.69(1?)	1.07(22)	0.94(16)
30	24.()		0.64(14)	0.91(15)
50	20.8		0.?0(6)	0.44(10)
70	18.7		0.11(2)	

§Values in parenthesis are l-sigma uncertainties in units of the last digit.
†Average of the profiles from 6 sunrise occultations.
*}'refile from sunrise occultation SR03.
‡Average of the profiles from 7 sunset occultations.

Figure Captions

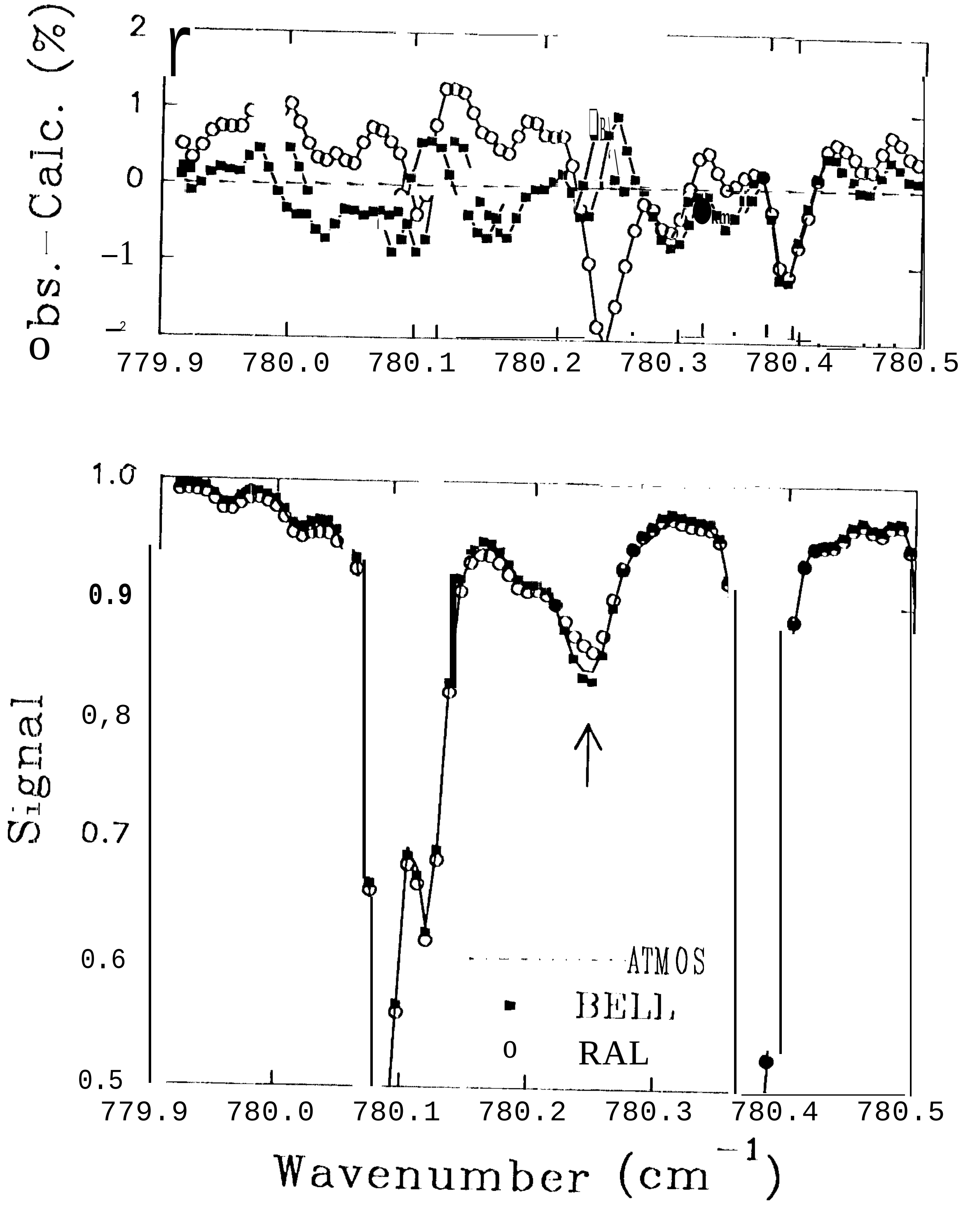
Figure 1. Comparison of spectral fitting results obtained with the new $ClONO_2$ line parameters described in section 3 (labeled BELL) and the empirical $ClONO_2$ line parameters derived from laboratory measurements at the Rutherford Appleton laboratory by Ballard et al. [1988] (labeled RAL). The observed spectrum was recorded on March 25, 1992, at a tangent pressure of 30.6 mb during occultation SR03 (28.2° S latitude). The arrow marks the approximate location of the maximum absorption by the $^{35}ClONO_2$ ν_4 band Q branch. The measured spectrum has been apodized with Norton and Beer [1976, 1977] function number 2.

Figure 2. Upper frame: Comparison of ATMOS $ClONO_2$ profiles retrieved near 47° S latitude from the 1985 Spacelab 3 and the 1992 ATLAS 1 spectra. The Spacelab 3 profile is a revised retrieval obtained from the single sunrise occultation recorded on May 1, 1985. The ATLAS 1 profile is the mean of the individual profiles retrieved for the 7 sunset occultations listed in Table 1. Error bars are estimated 1-sigma precision. Lower frame: AER 47° S latitude model calculations for day 90 of 1992, sunset (solid curves), day 120 of 1992, sunrise (long dashed curves), and day 120 of 1985 (short dashed curves). See text for details.

Figure 3. Comparison of the mean ATMOS/ATLAS 1 $ClONO_2$ tropical sunrise profile and AER model profiles calculated for day 90 of 1992 with heterogeneous chemistry and an aerosol surface area density profile from SAGE II for the same time period. Because of the high aerosol

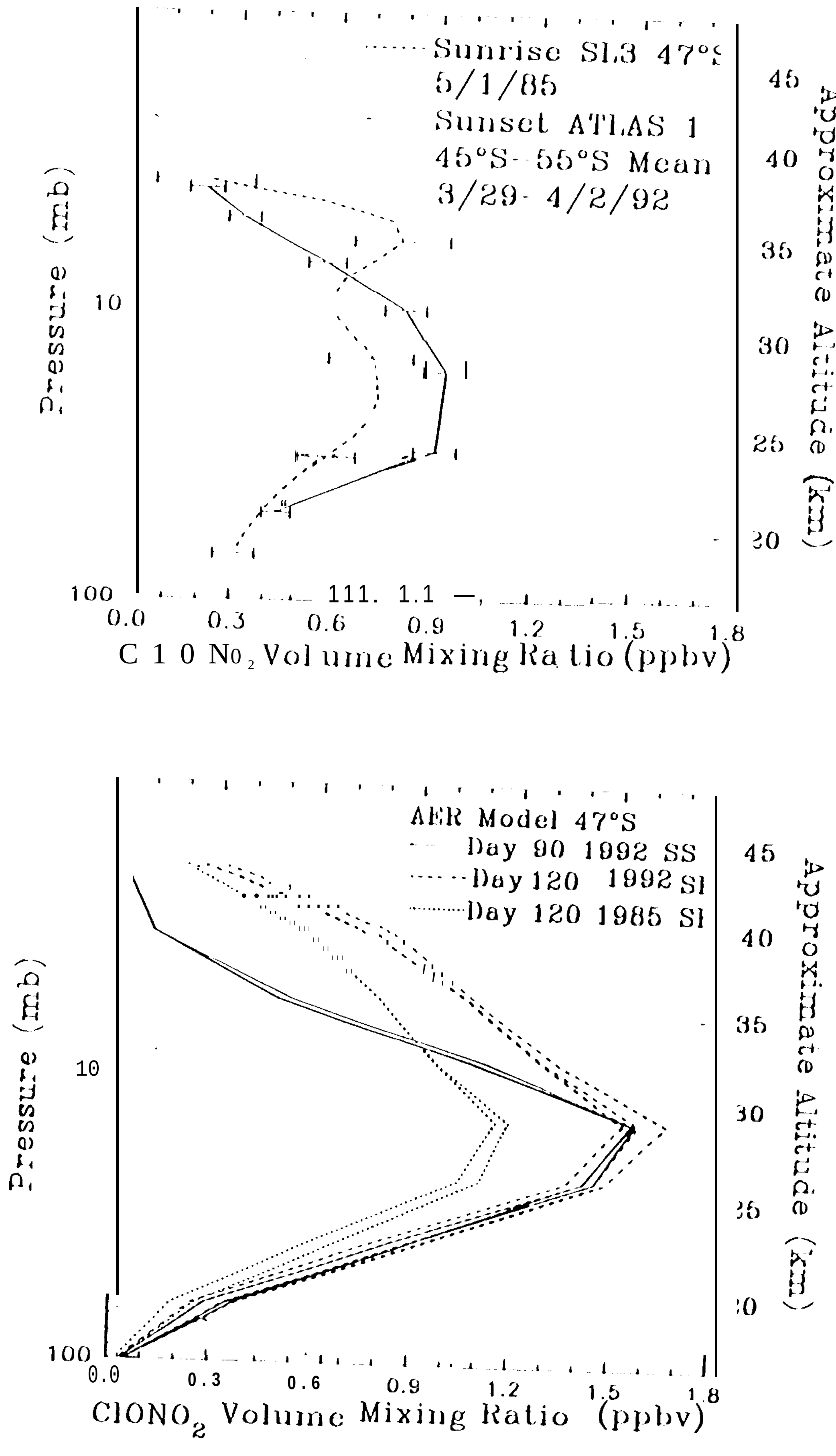
loading in the tropics from the Mt. . Pinatubo volcanic eruption of June 1991, no stratospheric observations were obtained below ~27 km altitude.

Figure 1



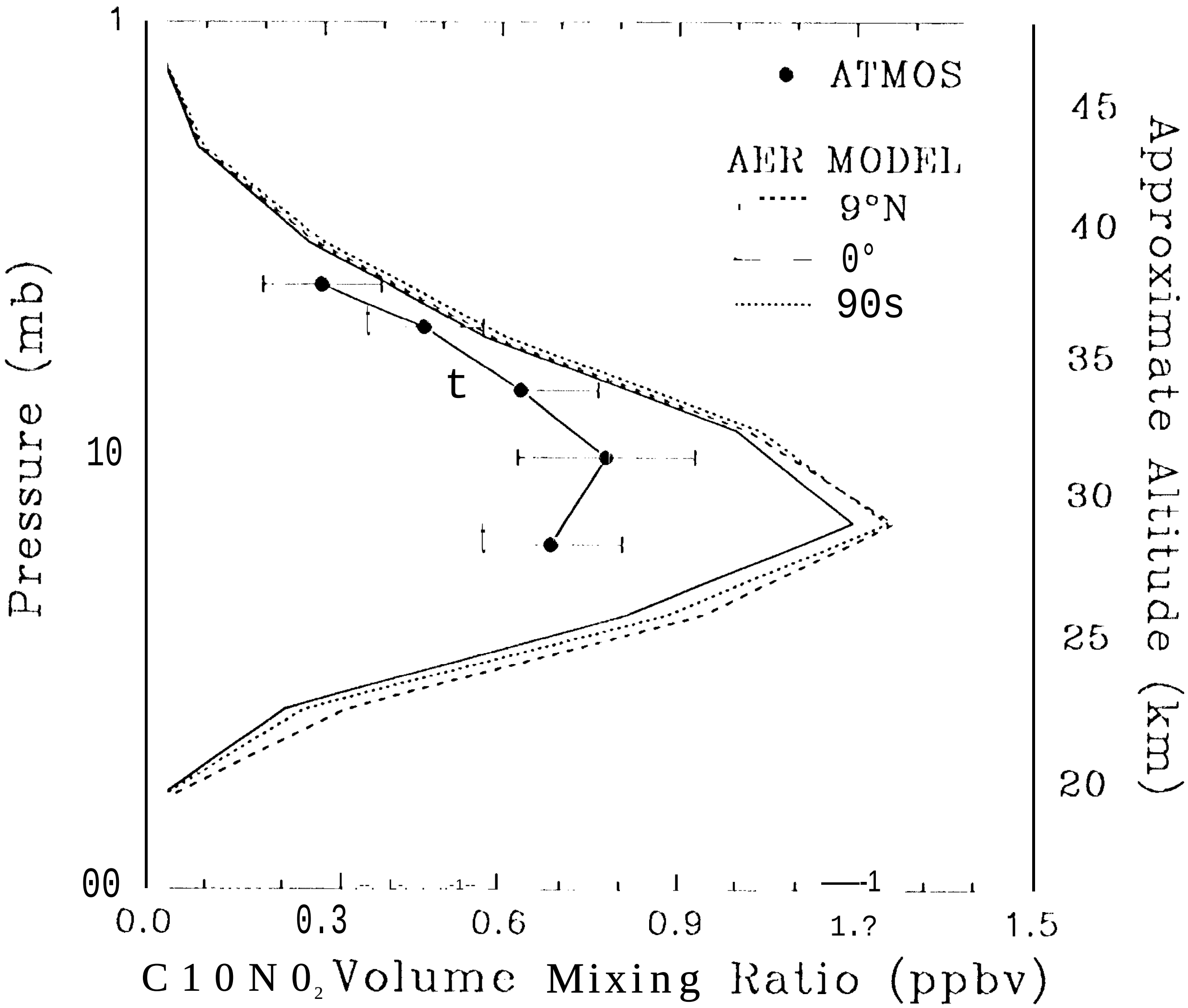
Obs. - Calc. (%)
2
1
0
−1
−2
779.9
780.0
780.1
780.2
780.3
780.4
780.5
1.0
0.9
0.8
0.7
0.6
0.5
Signal
ATMOS
BELL
RAL
Wavenumber (cm^{-1})

Figure 2



Sunrise SL3 47°S
5/1/85
Sunset ATLAS 1
45°S–55°S Mean
3/29- 4/2/92
Pressure (mb)
10
100
Approximate Altitude (km)
45
40
35
30
25
20
0.0
0.3
0.6
0.9
1.2
1.5
1.8
ClONO2 Volume Mixing Ratio (ppbv)
AER Model 47°S
Day 90 1992 SS
Day 120 1992 SI
Day 120 1985 SI
Pressure (mb)
10
100
Approximate Altitude (km)
45
40
35
30
25
20
0.0
0.3
0.6
0.9
1.2
1.5
1.8
ClONO2 Volume Mixing Ratio (ppbv)

Figure 3



ATMOS
AER MODEL
9°N
0°
90s
Pressure (mb)
1
10
00
Approximate Altitude (km)
45
40
35
30
25
20
0.0
0.3
0.6
0.9
1.?
1.5
C10N0₂ Volume Mixing Ratio (ppbv)

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